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The Electrochemistry of Azine, Oxazine and Thiazine Dyes

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Accomplishments

The role of short-lived intermediates of dyes such as methylene blue, safranin-O, neutral red and oxazines used in the photosensitization of electrodes was studied by means of laser flash photolysis and voltammetry. The study included transients initiated by absorption of light by dyes in solution and by dyes adsorbed on electrodes, with major emphasis on the transients arising from solution absorption. For each mode of photoexcitation the identity, the lifetime and the mechanism of formation and decay of the transient species was determined. Key variables examined systematically included pH, solvent composition, electrode material and potential, and reagents which selectively quench the excited state. The goal established the place of the formation and the disappearance of each transient species in the overall photoelectrochemical process.

Detailed transient studies as outlined in Technical Reports 2 and 4 provided information on decay pathways of semireduced dye intermediates. Establishment of the role of these short-lived intermediates was necessary for full understanding of the mechanism of photosensitization, and it should clarify the manner in which the structure and the photochemical properties of dyes influence the rates and energetics of the key steps of photoelectrochemical processes.

Multiple specular reflection was the basis of a new thin-layer spectroelectrochemical cell which does not use optically transparent electrodes, the optical sensitivity of which exceeds that of cells using transparent electrodes by a factor of several hundred. As a result, the ability to detect short-lived intermediates and weakly absorbing species in spectroelectrochemical studies is much improved. Absorbance changes less than 5×10^{-5}

absorbance unit per electrode reflection are readily observed. A cell 4 cm long with a 120- μ m spacing, operated to give approximately 330 reflections, was used to monitor optically the reduction of methylene blue and the reoxidation of the leuco form at concentrations as low as 5×10^{-7} M. Further details are shown in Technical Report No. 1.

Two secondary goals were to verify kinetic data where possible by independent methods and to study systematically the influence that adsorption of the dye has on the kinetics of the transient intermediates. We were particularly interested in the effect of such adsorption on the electrode kinetics of the transient intermediates, and thus the pathway and rate of the overall electrochemical process.

We applied the formal analysis developed by Laviron to azine, oxazine and thiazine dyes adsorbed on electrode surfaces. Technical Report 3 outlines the procedures employed in these studies. The development of electrochemically distinguishable phases under conditions of high surface coverage which was of special interest, appears to be associated with strong attractive interactions. In one case the redox potential and the acidity of the adsorbed dye differ significantly from those of the dye in solution.

The very long lifetimes of the semireduced and semioxidized radicals of many thiazine, azine and oxazine dyes in acetonitrile or dimethylsulfoxide enabled direct measurements to be pursued. Laser photochemistry of these dyes determined the lifetimes of the transients species and those with sufficiently long lifetimes were studied by cyclic voltammetry. Technical Reports 5 through 8 are being written and will provide the remaining details on the work performed under this contract.

CO-WORKERS

Charles E. Baumgartner - Ph.D. 1980

Gary T. Marks - Ph.D. 1982

Eric Lee - Ph.D. 1984

Vincent Abraham - Ph.D. (expected in 1985)

John Fitzsimmons - Graduate Student - (4th year)

Wayde Schmidt - Graduate Student - (3rd year)

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LIST OF REPORTS, PUBLICATIONS, ETC.

1. "Spectroelectrochemical Monitoring of Electrode Reactions by Multiple Specular Reflection Spectroscopy", C. E. Baumgartner, G. T. Marks, D. A. Aikens and H. H. Richtol, Anal. Chem., 52, 267 (1980).
2. "Transient Photochemistry of Safranin-O", C. E. Baumgartner, H. H. Richtol and D. A. Aikens, Photochemistry, Photobiology, 34, 17 (1981) (Technical Report No. 3).
3. "Linear Sweep Voltammetry of Adsorbed Neutral Red", S. Creager, D. A. Aikens, and H. H. Richtol, Journal of Electroanalytical Chemistry, 152, (1983), 197-209.
4. "Transient Photochemistry of Neutral Red", G. T. Marks, E. Lee, D. A. Aikens, and H. H. Richtol, Photochemistry, Photobiology, 39 (3), (1984), 323-328 (Technical Report No. 5).
5. "Linear Sweep Voltammetry of Adsorbed Safranin-O", V. Abraham, D. A. Aikens, and H. H. Richtol, Journal of Electroanalytical Chemistry, to be submitted.
6. "Transient Photochemistry of Methylene Blue in DMSO", E. D. Lee, D. A. Aikens, and H. H. Richtol, Journal of Physical Chemistry, to be submitted.
7. "Linear Sweep Voltammetry of Adsorbed Oxazine Dyes", W. Schmidt, D. A. Aikens, and H. H. Richtol, Journal of Electroanalytical Chemistry, to be submitted.
8. "Linear Sweep Voltammetry of Thionine and Methylene Blue in DMSO", J. Fitzsimmons, D. A. Aikens, and H. H. Richtol, Journal of Electroanalytical Chemistry, to be submitted.